

Final report on NASA grant NAGW-1734

**"Optical Properties of CO₂ Ice and CO₂ Snow
in the Ultraviolet, Visible, and Infrared"**

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Period covered: 1 June 1989 - 30 November 1992

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1. Final technical report.

This grant supported the work of Gary Hansen toward his Ph.D. thesis. Hansen is a graduate student in Geophysics at the University of Washington (UW), working in laboratory facilities provided by the Jet Propulsion Laboratory (JPL).

The project was to measure the optical constants of CO₂ ice in the spectral regions of weak absorption. Many previous measurements had been made by others in the strong absorption bands, but the weak regions had been poorly measured or not measured at all. In these regions the emissivity of CO₂ frost and CO₂ clouds is quite sensitive to particle sizes and to the value of the absorption coefficient, so the new measurements will have applications to energy budget and remote sensing of the Martian surface and atmosphere.

During the time period covered by this grant, Hansen developed a method for growing clear crystals of CO₂, 4 cm in length. He constructed apparatus for accurate measurement of spectral transmission through these crystals, for wavelengths 0.18-3.8 μ m, covering the near-ultraviolet, visible, and near-infrared regions, bounded by the strong ultraviolet absorption and the 4.3- μ m band. Our new best estimate of the spectral absorption

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coefficient (expressed as imaginary refractive index) is shown in Figure 1. It is a composite result of many measurements on dozens of crystals.

Now that we have a good dataset for the shortwave absorption spectrum, the focus of the research has moved to the thermal infrared, for which Hansen has adapted a Fourier Transform interferometer for use with CO₂-ice crystals.

This project was also supported in part by JPL, and by the Caltech President's Fund, and by a UW Space Grant fellowship.

2. Publications.

Published abstracts for three conference proceedings are attached.

Hansen, G.B., 1991: The spectral absorption of CO₂ ice in the ultraviolet, visible, and near-infrared. *Bull. Am. Astron. Soc.*, 23, 1176.

Hansen, G.B., 1992: The spectral absorption of CO₂ ice from 0.18 to 4.8 mm. *Bull. Am. Astron. Soc.*, 24, 978.

Hansen, G.B., and T.Z. Martin, 1993: Modeling the reflectance of CO₂ frost with new optical constants: application to Martian south polar cap spectra. *Lunar and Planetary Science Conference*, 24, 601-602.

3. Final Property Inventory.

The final property inventory will be sent separately to NASA.

4. Final Patent/Invention Report.

No patents or patent applications resulted from research on this grant.

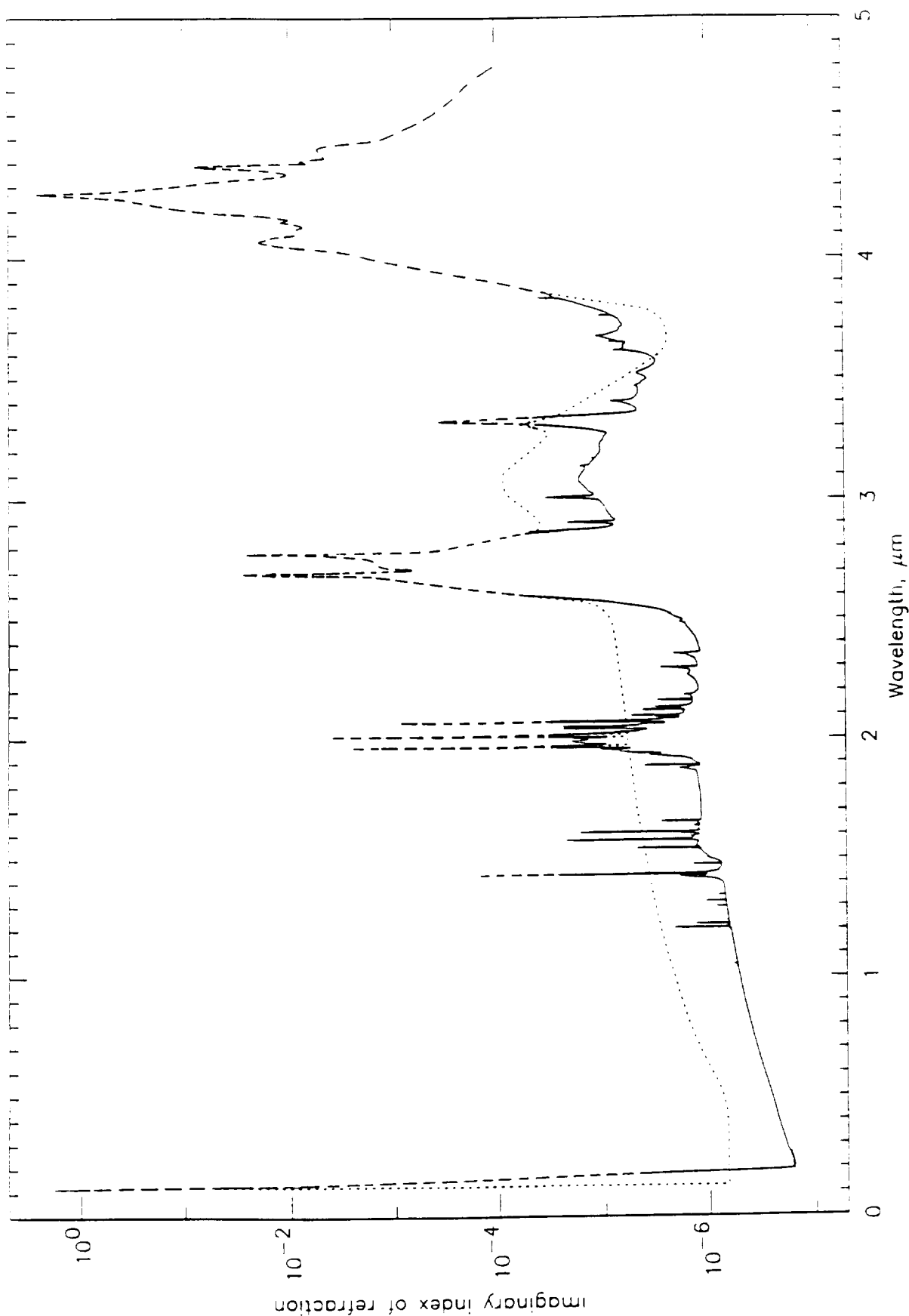


Figure 1: Current best estimate of the imaginary index of refraction of CO₂ ice in the ultraviolet, visible, and near-infrared. The solid portions are the weakly absorbing regions measured in this study and the dashed portions are the strongly absorbing regions which were available from earlier studies. The dotted lines are earlier estimates reviewed by Warren (1986) which are superseded by our new measurements. This plot shows the best compilation at the time the grant ended. The region 1.5-2.4 μm has been subsequently remeasured; the background is lower than shown here.

13.14-P

The Spectral Absorption of CO₂ Ice in the Ultraviolet,
Visible, and Near-infrared

G.B. Hansen (Univ. of Washington/JPL)

A significant fraction of the CO₂ atmosphere of Mars annually condenses onto its surface. Understanding this annual cycle of CO₂ and its long-term variation is key to understanding the Martian climate. The use of remote sensing to investigate the formation and sublimation of CO₂ clouds and polar caps on Mars is limited, however, by inadequate knowledge of the absorption coefficient and refractive index of CO₂ ice as functions of wavelength, particularly in the weakly absorbing parts of the CO₂ spectrum.

While the desired properties of CO₂ ice can, in principle, be determined in the laboratory, past measurements (reviewed by Warren, *Appl. Opt.*, **25**, 2650, 1986) have been limited by the difficulty of growing clear crystals of CO₂ ice large enough to obtain measurable absorption.

Over the last two years, a method of growing large, clear samples of CO₂ ice at temperatures of 150-160K has been developed. An adaptable chamber has been built for growing samples from 1.6mm to 107mm thick. The optical system has been set up to measure absorption compared to a reference path from 0.15 μ m to 4.8 μ m with 0.1-2.0nm resolution.

Preliminary measurements in the near-infrared (1.2-1.6 μ m) show a substantially transparent background (path length 13mm) punctuated with many narrow absorption lines of about 2nm width, including some weak ones which have not been observed in thin films or frosts.

Calibrated spectral measurements are now beginning, progressing across all wavelengths at each thickness. Optical absorption will be estimated at some wavelengths after at least two thicknesses have been measured. These data will be applied to models for the albedo or emissivity of frosts as illustrated in Warren, et al., *J. Geophys. Res.*, **95**, 14717, 1990.

This is a cooperative project of the University of Washington, Seattle, and JPL.

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The Spectral Absorption of CO₂ Ice from 0.18 to 4.8 μ m

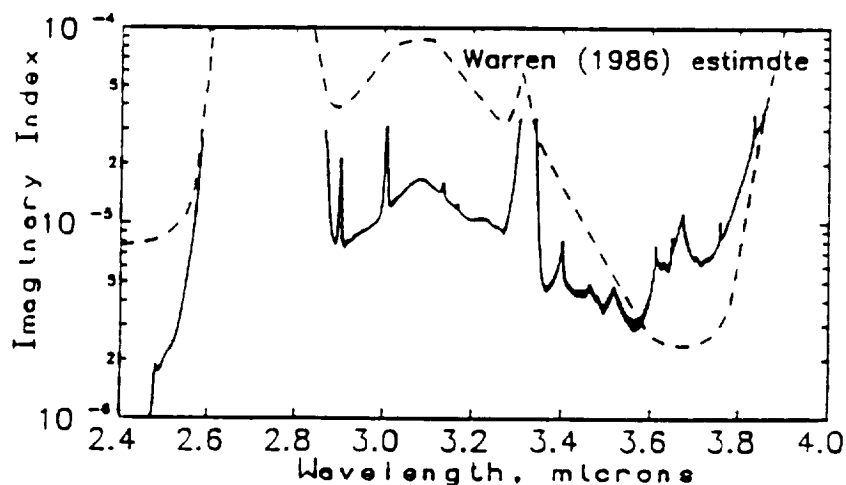
G.B. Hansen (Univ. of Washington/JPL)

Accurate absorption coefficients of CO₂ ice, especially in spectral regions of weak absorption between the strong bands, are needed to understand the absorption, transmission, reflection, and emission of radiation by CO₂ snow and CO₂ clouds (Warren, et al., *J. Geophys. Res.*, 95, 14717, 1990).

The spectral absorption coefficient is being obtained in these weak regions by measuring transmission through samples more than 10 mm thick, as described by Hansen, *Bull. Amer. Astron. Soc.*, 23, 1176.

The ultraviolet absorption edge was found at 183 nm. Data have been collected from that wavelength to 4.8 μ m, except in the strongest absorption bands. An example from 2.4 to 3.9 μ m is shown in the figure, compared to the data of Dittion and Kieffer, *J. Geophys. Res.*, 84, 8294, 1979 (as reanalyzed by Warren, *Appl. Opt.*, 25, 2650, 1986), which it supersedes.

This is a cooperative project of the University of Washington, Seattle, WA, and the Jet Propulsion Laboratory, Pasadena, CA, and is supported partly by a grant from NASA and partly by the Caltech President's Fund.



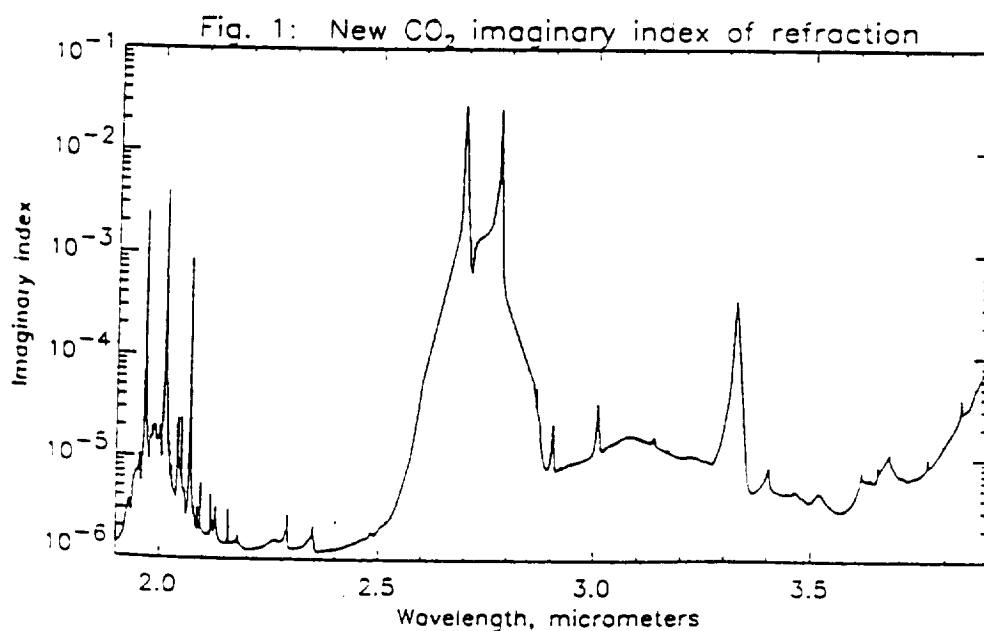
**MODELING THE REFLECTANCE OF CO₂ FROST WITH NEW OPTICAL CONSTANTS:
APPLICATION TO MARTIAN SOUTH POLAR CAP SPECTRA; Gary B. Hansen, Univ. of Wash./Jet
Propulsion Lab 183-601, Pasadena, CA 91109; Terry Z. Martin, Jet Propulsion Lab 169-237, Pasadena, CA
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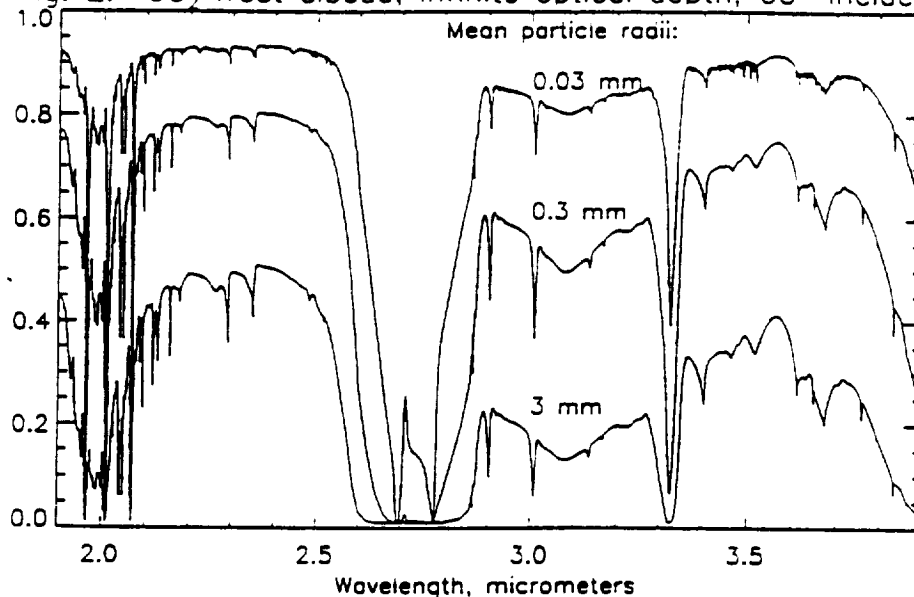
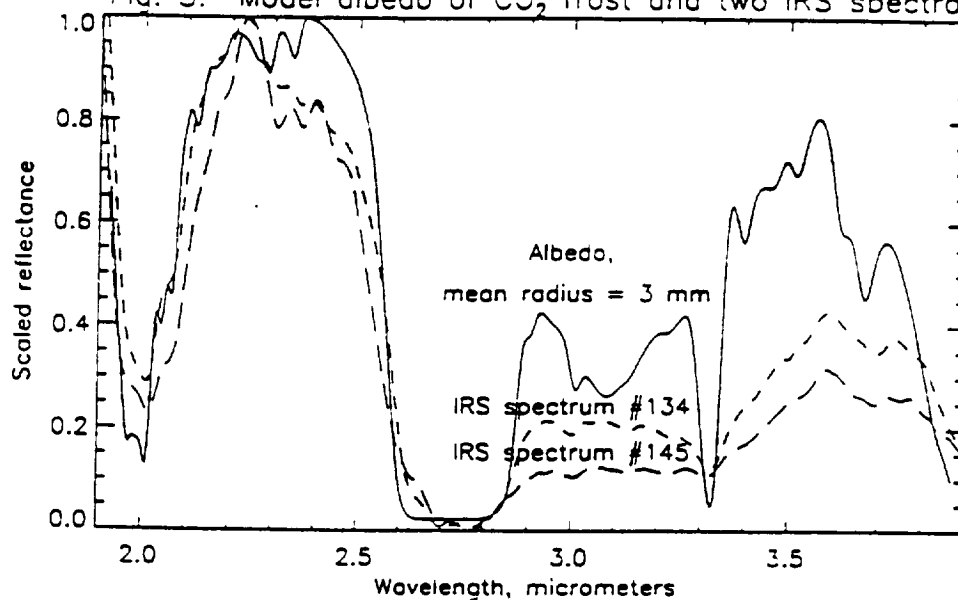
New measurements of the absorption coefficients of CO₂ ice, in most of the spectral range 0.2 to 3.9 μm where absorption coefficients are below 1.5 per cm, have recently been made [1]. Although these measurements are preliminary, they contain spectral detail not seen previously in the literature. Therefore, it is useful to combine these new data with older data from spectral regions of stronger absorption [2] and reformulate models of the albedo [3] or reflectance [4] of CO₂ frost. These models can then be adjusted in an attempt to match measurements of Martian polar deposits, such as the set of spectra returned by the IRS instrument on Mariner 7 (1969) [5,6].

The new absorption coefficients of CO₂ ice were measured on several samples of 41-mm thickness at 150-155 K. A portion of the spectrum from 1.9 to 3.9 μm wavelength is shown in Figure 1 in the form of imaginary coefficient of refraction ($=$ linear absorption \times wavelength $/ 4\pi$). The data above about 3×10^{-5} are obtained from [2], except for the absorption line at 3.32 μm , which is extrapolated in a way that is consistent with laboratory frost measurements [7], but the peak level is still highly uncertain.

This new imaginary coefficient, combined with the real coefficient from [2], can be immediately applied to the models for hemispherical albedo used in [3], resulting in markedly different results from those in that study. The results for an infinite optical depth layer and solar incidence of 60° are plotted in Figure 2 for a range of mean particle radii from 0.03 to 3 mm.

Although this is an albedo model and not a bidirectional reflectance model, it can still be qualitatively compared to measured spectra of the Martian polar cap, such as the set of near- to middle-infrared spectra taken of the south polar cap in spring ($L_S = 200^\circ$) by the IRS instrument on Mariner 7. The albedo model degraded to the resolution of the IRS is compared to two of these spectra in Figure 3. They are scaled to 1.0 at their maximum reflectance near 2.2 μm . The regions from 2.2 to 2.6 and from 3.0 to 3.9 μm are substantially free of atmospheric gas absorptions and can be compared directly. Note the coincidence of the characteristic absorption features of the ice at 2.28, 2.34, 3.00, 3.32, and 3.67 μm , and the albedo/reflectance maximum at 3.57 μm . (The wavelength calibration used for the IRS spectra is not yet accurate for the 2.2-2.6 μm region.)



NEW MODEL REFLECTANCE OF CO₂ FROST: Hansen, G.B., and T.Z. MartinFig. 2: CO₂ frost albedo, infinite optical depth, 60° incidenceFig. 3: Model albedo of CO₂ frost and two IRS spectra

The use of a reflectance model as well as the addition of water ice and/or dust contamination will be addressed in an effort to better match the observed spectra in this data set. In particular, the maximum at 2.2 μm , the slope from 2.3-2.6 μm , and the depression and muting of features at wavelengths longer than 2.9 μm are characteristic of water ice contamination as illustrated in [3].

This is a cooperative project of the University of Washington, Seattle, WA, and the Jet Propulsion Laboratory, Pasadena, CA, and is supported partly by a grant from NASA and partly by the Caltech President's Fund.

REFERENCES: [1] Hansen, G.B. (1992), *BAAS*, 24, 978. [2] Warren, S.G. (1986), *Appl. Opt.*, 25, 2650. [3] Warren, S.G. et al. (1990), *JGR*, 95, 14717. [4] Calvin, W.M. (1990), *JGR*, 95, 14743. [5] Pimentel, G.C. et al. (1974), *JGR*, 79, 1623. [6] Martin, T.Z. (1993), *JGR*, in press. [7] Fink, U. and G.T. Sill (1982), in *Comets*, L.L. Wilkening, ed., U. of Arizona Press, Tucson, 164.